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Methylmercury Binding Sites in Humic Substances: X-ray Absorption Study

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Methylmercury, a highly toxic and bioaccumulative form of mercury, is known to have a strong affinity for binding to organic matter in soil, sedimentary, and aquatic environments. The objective of our study was to determine the dominant ligands that bind to the methylmercury cation (CH_3Hg^+) in humic acids (complex organic compound mixtures) by evaluating several CH_3Hg^+-ligand complexation models. Mercury L_{III}-edge extended x-ray absorption fine structure (EXAFS) results show that CH_3Hg^+ preferentially binds to thiol ligands (—SH), also known as sulfhydryl. After saturating reactive thiol ligands, the remaining CH_3Hg^+ binds to carboxyl ligands rather than to amine or reduced-sulfur ligands other than thiol.

In organisms, such as fish, the dominant form of accumulated mercury is the organometallic methylmercury cation CH_3Hg^+, rather than the inorganic cation Hg^{2+}. Scientists have reported that the biotic and abiotic methylation of inorganic mercury is affected by natural organic matter. Humic substances, for example, either stimulate mercury methylation, acting as methyl donors for Hg^{2+}, or suppress it by forming complexes with Hg^{2+}. Examining the nature of organic and inorganic mercury complexes with natural organic matter is important for understanding the biogeochemical cycle of mercury as well as the fate of mercury in the environment.

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Both Hg^{2+} and CH_3Hg^+ have strong affinities for organic matter in terrestrial and aquatic environments, with CH_3Hg^+ having a lower affinity than Hg^{2+}. The principle of hard and soft acids and bases (the HSAB principle) predicts the strong affinity of reduced-sulfur ligands for Hg^{2+} and CH_3Hg^+. Previous mercury L_{III}-edge extended x-ray absorption fine structure (EXAFS) studies show that humic sulfur ligands bind both Hg^{2+} and CH_3Hg^+. Scientists, however, have reported that only a small fraction of reduced sulfur in humic substances binds to CH_3Hg^+, with oxygen or nitrogen binding to the remaining CH_3Hg^+. They speculated that CH_3Hg^+-binding sulfur ligands were, most likely, thiol and possibly sulfide, disulfide, and hydrogen disulfide groups. In this study, we determined the major CH_3Hg^+-binding humic ligands using mercury L_{III}-edge EXAFS. Our spectra were obtained at NSLS beamlines X11A and X10C.

We examined several CH_3Hg^+-ligand models as potential CH_3Hg^+-binding structures in humic acids: thiol (—SH), sulfide (—S—), disulfide (—SS—), hydrogen polysulfide (—SSH or —SSSH), carboxyl (—COOH), and amine (—NH_2). We examined carboxyl and amine ligands, although they are hard Lewis ligands, because CH_3Hg^+-amine complexes exhibit relatively high complexation constants, and carboxyl is the most abundant ligand in humic acids.

We equilibrated two different humic-acid solutions (soil and aquatic) at CH_3Hg^+-to-reduced-sulfur ratios ranging from 0.3 to

1.5, quantifying the reduced-sulfur (e.g., thiol, sulfide, and hydrogen polysulfide) content using sulfur K-edge x-ray absorption near edge structure (XANES) spectroscopy at beamline X19A.

Our results show that thiol is the dominant CH_3Hg^+ complexing ligand among the reduced sulfur ligands (**Figure 1**). We did not observe EXAFS evidence of CH_3Hg^+ complexation to sulfide, disulfide, or hydrogen disulfide ligands in any of our samples. CH_3Hg^+ complexation by carboxyl ligands (**Figure 2**) becomes significant after CH_3Hg^+ saturates the available thiol ligands. Carboxyl ligands, rather than amine, eclipse thiol ligands as the CH_3Hg^+-to-reduced-sulfur ratio approaches and then exceeds 1. We also found evidence for proximately coordinated heavy atoms in a sample where the CH_3Hg^+-to-reduced-sulfur ratio slightly exceeded 1. The heavy-atom backscattering behavior agrees the best with that of mercury or, possibly, other atoms with similar atomic numbers.

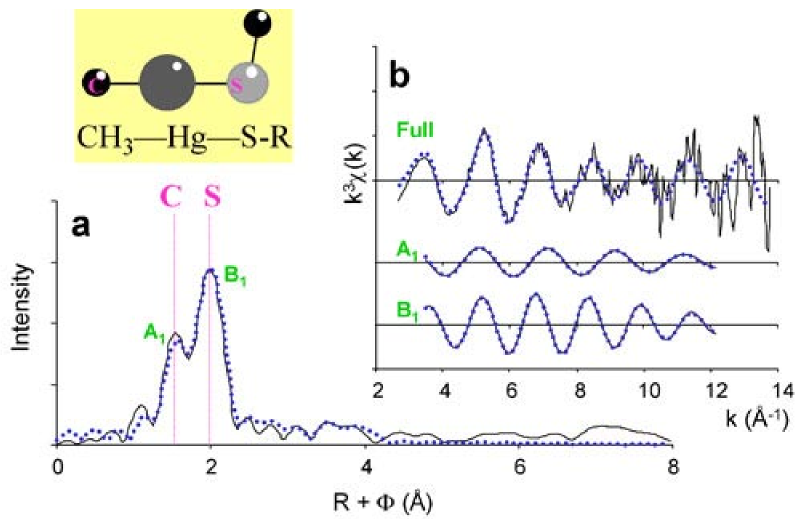

Figure 1. *Experimental (solid lines) and least-squares fitted (dotted lines) Hg L_{III}-edge EXAFS of CH_3Hg^+-humic thiol complex (aquatic humic acid; CH_3Hg^+ to reduced sulfur ratio, 0.3, pH 5): (a) radial structure function and (b) EXAFS scattering curves (full scattering curve and Fourier-filtered scattering curves of peak A_1 and peak B_1).*

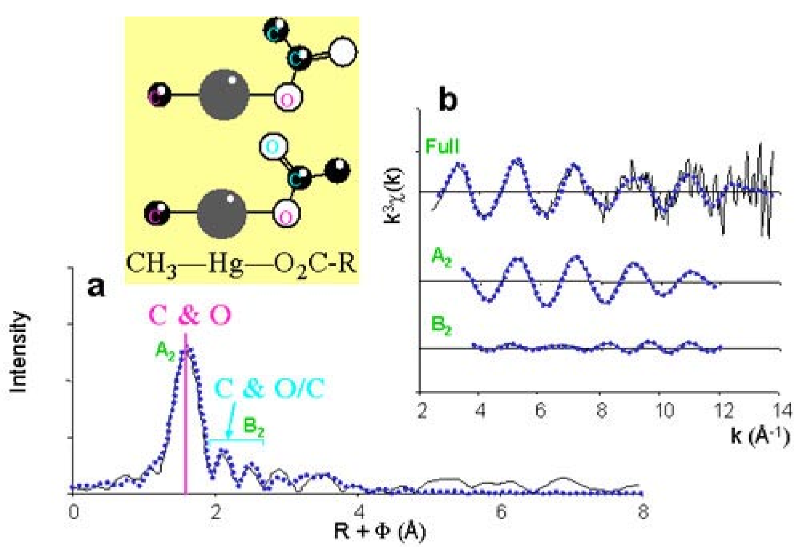

Figure 2. *Experimental (solid lines) and least-squares fitted (dotted lines) Hg L_{III}-edge EXAFS of CH_3Hg^+-humic carboxyl complex (soil humic acid; CH_3Hg^+ to reduced sulfur ratio, 1.3, pH 4): (a) radial structure function and (b) EXAFS scattering curves (full scattering curve and Fourier-filtered scattering curves of peak A_2 and scattering region B_2).*